A STUDY OF CERTAIN SELENIUM COMPOUNDS AND THEIR APPLICATION TO ANALYTICAL CHEMISTRY

by

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INTRODUCTION

This research problem consisted of two parts. The first part was a study of the methods for the preparation of selenic acid. The second part was the development of a procedure using potassium selenocyanate for the quantitative determination of cobalt.

Selenic acid was first prepared in 1827 (3) by suspending lead selenate in water and then precipitating the lead with hydrogen sulfide. The lead selenate was prepared by fusing selenium dioxide with potassium nitrate. Insoluble lead selenate was formed when lead nitrate was added to a dilute solution of the fusion. This precipitate was thoroughly washed with water after which it was suspended in water and treated with hydrogen sulfide. The lead sulfide thus obtained was removed by filtration, and the resulting dilute solution concentrated by boiling under diminished pressure. Selenic acid was also prepared by suspending other metal selenates in water and precipitating the metal with an appropriate reagent.

Selenic acid can be prepared by the anodic oxidation of selenium dioxide. The cathode solution is 5 N nitric acid, with 35 grams of selenium dioxide in 50 cc of water for the anode solution (7). However, the selenic acid thus prepared is contaminated by nitric acid.

Selenic acid may be prepared also in over 90 per cent yield by the oxidation of selenium to selenium dioxide with nitric acid (9), and then heating the solution with chloric acid (from barium chlorate and sulphuric acid) to not above 170° and finally in vacuo. From this method the final product may contain traces of chloride compounds and $Ba(HSeO_4)_2$.

None of the above methods is practical for the preparation

selenic acid because they give products contaminated with foreign ions. However, the following procedure produces relatively pure selenic acid.

Meyer and Heider produced selenic acid by treating selenium dioxide with 30 per cent hydrogen peroxide and warming the mixture on a water bath. Forty-eight per cent of the oxide oxidized to selenic acid. With larger amounts of peroxide 70 per cent was oxidized. Gibbertson and King (5) improved the above method by adding 300 per cent excess peroxide and allowing the mixture to stand for 24 hours before refluxing in an all-glass apparatus for 12 hours. In this way a 90 per cent yield could be obtained. The peroxide and most of the water were removed by distillation on a steam bath under reduced pressure.

The preparation of selenious acid is a rather standard procedure. Red or powdered gray selenium is slowly added to concentrated nitric acid. The mixture is then evaporated to dryness. The crude selenium dioxide can be purified by dissolving in water and hydrochloric acid and reprecipitating the selenium with sulfur dioxide. The purified selenium is then carried through a repetition of nitric acid oxidation. An alternative method is to sublime the selenium dioxide away from the less-volatile oxides of impurities (1).

The above review of the literature showed that there was only one method available for the preparation of pure selenic acid. However, in this one procedure a 300 per cent excess of hydrogen peroxide was necessary. The present investigation was undertaken in ord to study the use of potassium permanganate and hydrogen peroxide as oxidizing agents for the preparation of pure selenic acid. T

foreign ions produced in these reactions were removed by passing the solutions through a suitable resin.

The second part of the work concerns the complexes of cobalt with potassium selenocyanate. Very little work has been done with potassium selenocyanate. By comparing the properties of selenium compounds with the corresponding sulfur compounds, one would expect selenocyanate ion to form complexes with cobalt similar to those formed by cobalt and the thiocyanate ion. West and DeVries (15) mention that a cobalt-selenocyanate-water system has an absorptancy peak at 510 mu. In a mixed media there was a special absorptancy peak at 620 mu. Since a preliminary laboratory test showed that an intense blue color was produced by the cobalt selenocyanate complex, this colored complex was investigated to determine if it could be used for a quantitative determination of cobalt. The Beckman spectrophotometer was used to measure the intensity of the colored complex.

EXPERIMENTAL

Preparation of Selenic Acid

The first step in the preparation of selenic acid was to prepare a standard solution of selenious acid. This was done by placing an excess of concentrated nitric acid in a porcelain evaporating dish, heating and slowly adding gray selenium, allowing it to dissolve. The mixture was then evaporated to dryness. The selenium dioxide was dissolved in distilled water and the mixture again evaporated to dryness to remove any excess nitric acid. The purif

salt was dissolved in water and placed in a glass stoppered flask.

The selenious acid was standardized by titrating it against a solution of sodium hydroxide of known normality. Methyl orange was used as an indicator in the beginning but since it was difficult to recognize the end point we changed to tetrabromo-m-cresol-sulfonphthalein (bromo-cresol-green). This gave a better end point. A pH plot of the selenious acid titration is given in Fig. 1. A Beckman pH meter Model M was used for the pH determinations. Selenious acid has two pH breaks, one at a pH of 4.4-6.1 and the second one at a pH of 10-11.

For the first runs of the oxidation of selenious acid with potassium permanganate, an excess of 100 per cent the permanganate was used. The weighed amount of potassium permanganate was added to a small volume of selenious acid. The mixture was stirred for an hour and a half and then heated to 80-95° for 15 minutes. The reddish-brown precipitate was allowed to settle before the solution was filtered. A Buchner funnel and Whatman 42 filter paper were used for the filtration. The precipitate was washed and the solution diluted to volume. To remove the potassium and manganese ions the solution of selenic acid was passed through a column containing an ion exchange resin.

The resin used was Amberlite IR 100.[1] The column was prepared by placing pyrex glass wool in the bottom of a 50-milliliter burette, suspending the resin in a water solution and adding it to the burette.

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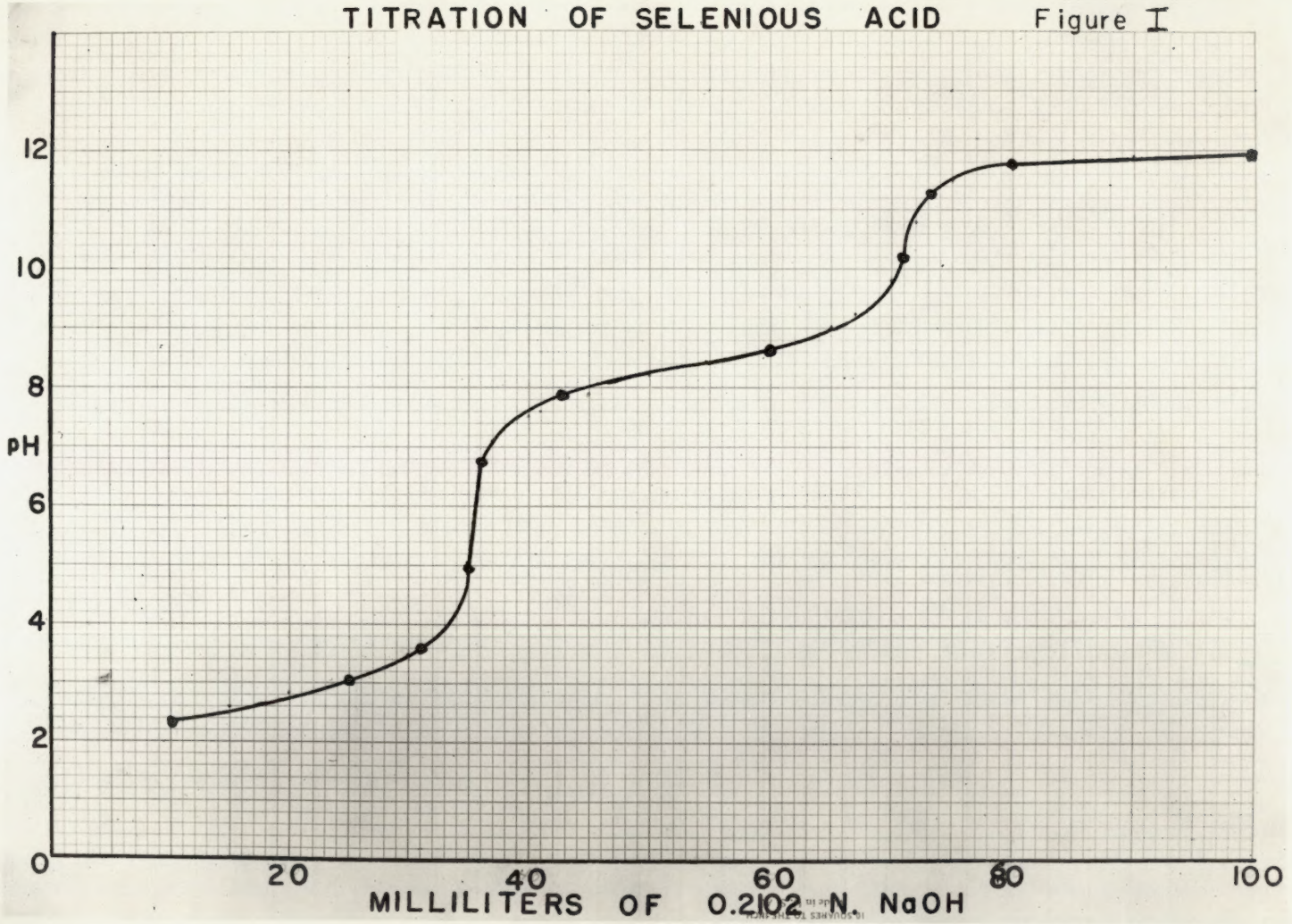
[1]Resin furnished by Rohn and Hass Company, Philadelphia, Penn


TITRATION OF SELENIOUS ACID
Figure I
12
10
8
pH
6
4
2
0
20
40
60
80
100
MILLILITERS OF 0.2102 N. NaOH

The resin settled to the bottom of the burette and the excess water was drained off as more of the suspended resin was added until a column of desired height was reached. The resin was then charged with hydrogen ions by slowly passing a five per cent solution of hydrochloric acid through the column. The amount of acid needed was determined by experience. After the acid was run slowly through the resin it was washed with distilled water to remove the excess hydrochloric acid and the chloride ions. The effluent was checked with silver nitrate to make sure that all the chloride ions had been removed from the resin. The water level was kept above the level of the resin that no air bubbles would form in the resin. Air bubbles cause channelling and cut the efficiency of the resin.

The selenic acid solution was added to the column and allowed to pass slowly through the resin. As it passed through the resin the hydrogen ions were replaced by those of potassium and manganese. The resin had a greater affinity for the manganese, then potassium, and a greater affinity for the potassium than for the hydrogen ion due to the relative charges and ionic radii of the ions entering into the exchange. Enough water must be added to wash the last of the selenic acid from the resin. It is of course necessary to keep within the capacity of the resin or some potassium ions will be found in the solution.

To check the efficiency of the resin a spectrographic analysis was run on the selenic acid solution. A Bausch and Lomb large littrow spectrograph was used. The selenic acid solution had been separated into four five-milliliter portions as it came from the resin, and was shown to contain, for all practical purposes, no

manganese ions. The flame attachment was used to prove that there were no potassium ions present. On a five-milliliter portion that was not run through the resin both manganese and potassium ions were found to be present in large quantities.

The reddish-brown precipitate was soluble in hydrogen peroxide. The precipitate was analyzed for manganese, selenium and selenate. It was weighed into three samples and dissolved in 30 per cent hydrogen peroxide. To precipitate the manganese the solution was heated to boiling and concentrated ammonium hydroxide was added slowly until the solution was slightly basic to litmus paper; after five to ten minutes, the hot solution was filtered through Whatman 42 filter paper. The filtrate was checked with ammonium hydroxide for complete precipitation. The paper was placed in a weighed crucible, charred and ignited. The precipitate was weighed as a mixed oxide (Mn_3O_4).

The selenate ion was precipitated as silver selenate. Silver selenate is much less soluble than silver sulphate at a pH of 6-7, and as little as 10^{-3} milligrams of sodium selenate suffices to give a precipitate (11). An excess of silver nitrate was added to the hydrogen peroxide solution of the precipitate and silver selenate precipitated. The silver selenate was filtered in a weighed sintered-glass crucible and the filtrate checked for more selenate ion with additional silver nitrate. The precipitate was washed with acetone, dried at 110° and weighed as silver selenate. The moles of selenate present were then calculated.

For the precipitation of selenium, the peroxide solution was made strongly acid (6 N) with hydrochloric acid and an excess of

solid sodium sulfite was added. The red selenium was filtered through a weighed sintered-glass crucible and washed with water. The filtrate was checked by adding more hydrochloric acid and sodium sulfite. The selenium was dried at 110° and the moles of selenium present calculated. The red selenium changed to the gray form on heating. For best results the peroxide solution should be concentrated as much as possible before adding the acid and sodium sulfite.

By comparing the moles of manganese, selenium and selenate it was possible to suggest a formula for the precipitate. It is believed that the precipitate was manganic selenate. However, when larger excesses of potassium permanganate were used it seemed that some manganese dioxide appeared. This amount was small and the weight of the manganic selenate remained about the same.

This method of preparing selenic acid was not regarded as feasible since the appearance of an appreciable amount of manganic selenate in the precipitate would cause the yield of selenic acid to be too small.

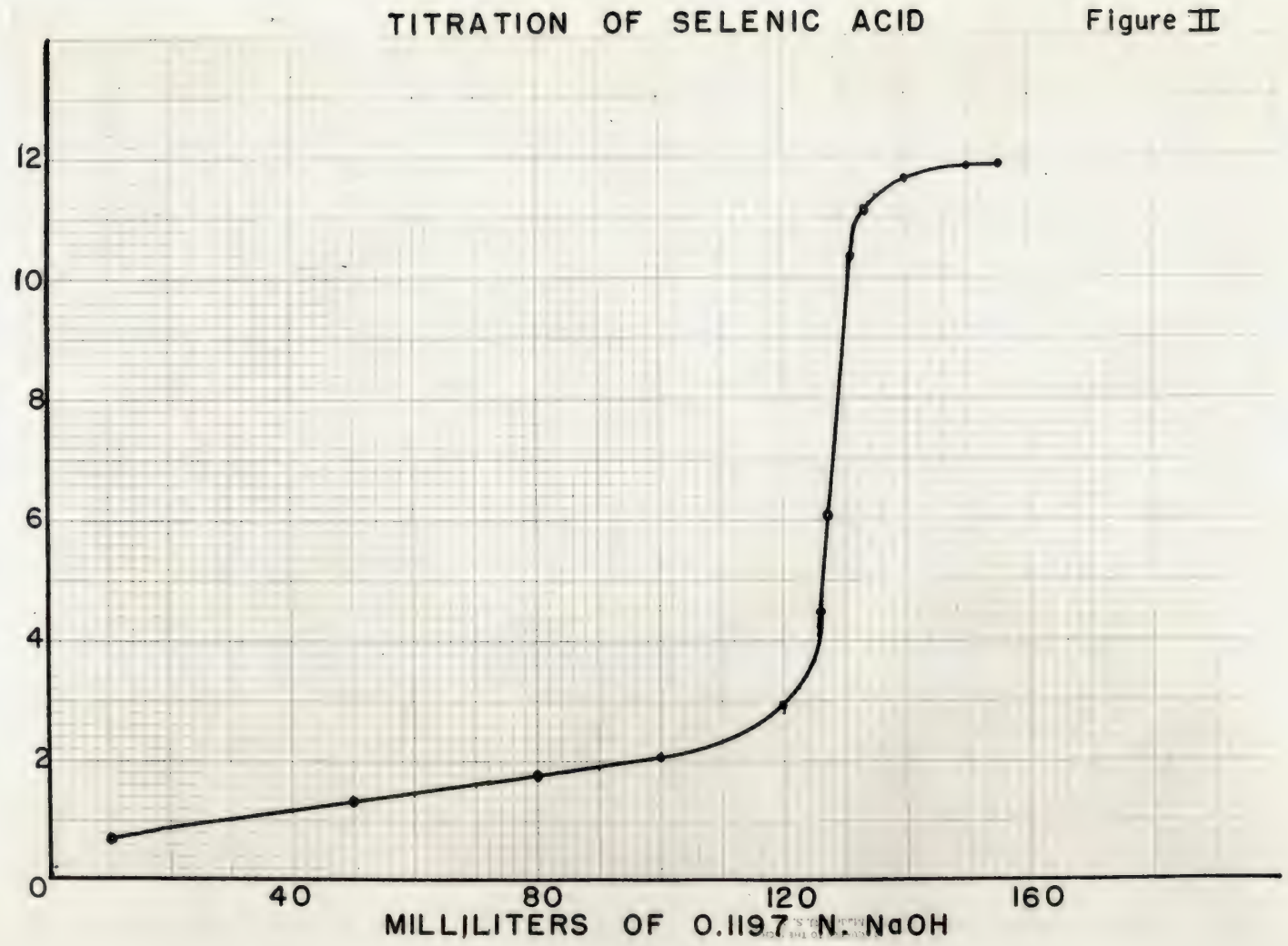
It was decided to improve the hydrogen peroxide method of preparing selenic acid by cutting down on the large (300 per cent) excess of hydrogen peroxide used in earlier work. The earlier method was run in an acid solution. A known amount of selenious acid was brought to a pH of 7.5 to 8.3, with ammonium hydroxide. An excess of 100 per cent of three per cent hydrogen peroxide was slowly added with stirring to the basic solution. There was an increase of about 20 degrees in the temperature indicating that the reaction was exothermic in nature. The mixture was allowed to stand about three hours and then evaporated to half its volume to remove excess

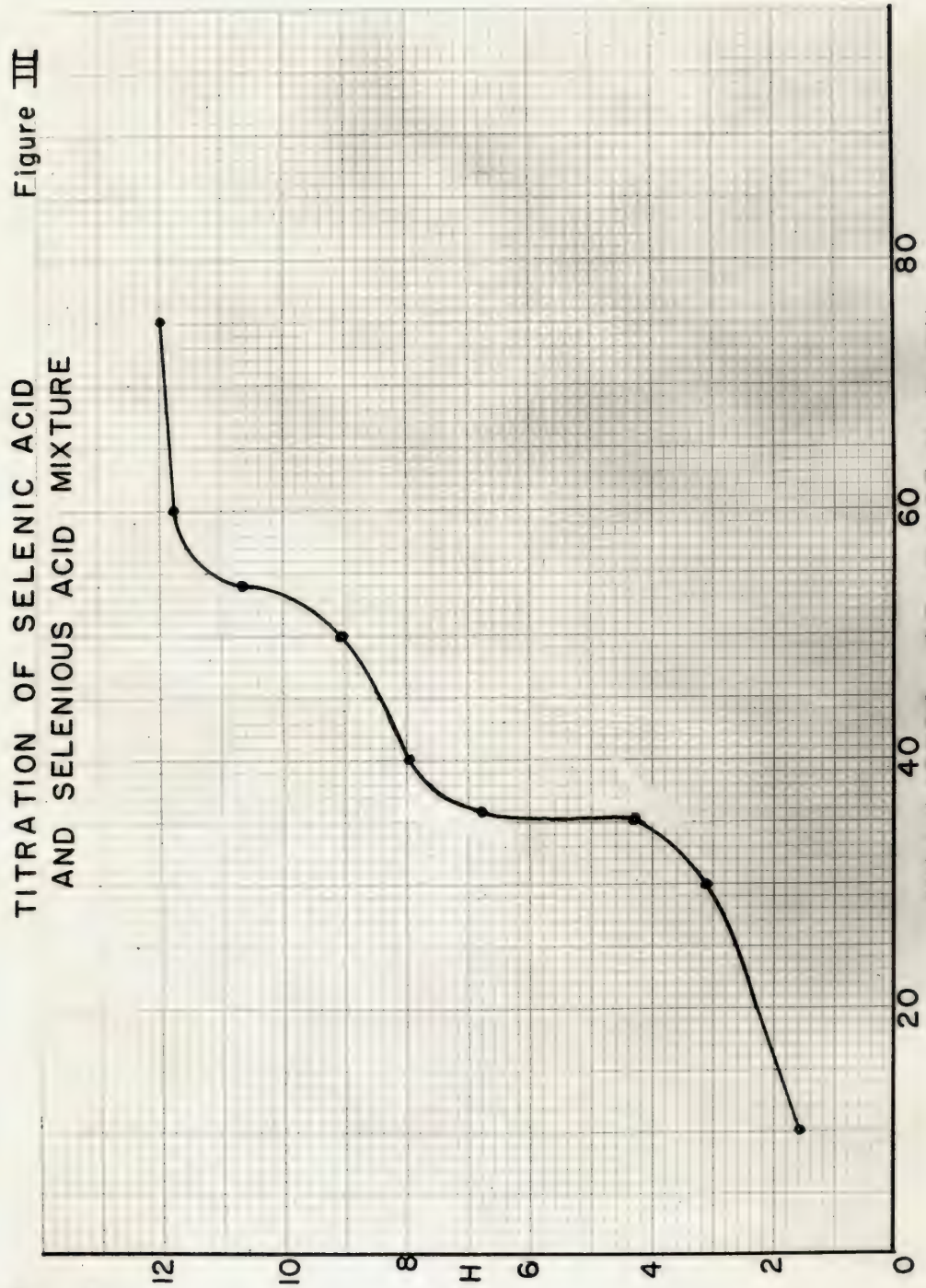
hydrogen peroxide or ammonium hydroxide. The solution was then run through the ion exchange resin to remove the ammonium ions present.

A modified Kjeldhal method was used to determine the effectiveness of the resin. Ten milliliters of the selenic acid was placed in a 100-milliliter Kjeldhal flask and made strongly basic with concentrated sodium hydroxide. Ten milliliters of 0.1 N sulfuric acid was used to catch the vapors and distillate. The sulfuric acid was then back titrated with dilute sodium hydroxide. It was shown that the ion exchange resin Amberlite IR 100 was ineffective for removing the excess ammonium ions present in the selenic acid solution.

It was necessary, therefore, to find a resin with a higher capacity for ammonium ions. This was done by preparing columns of different resins, as described before, and passing 100 milliliters of one molar ammonium chloride solution through the resin, collecting it in 10-milliliter samples and using the Kjeldhal method to check the effluent. The ion exchange resin Amberlite IR 120 was chosen.

After the selenic acid solution had been passed through the new resin and checked for ammonium content it was standardized by titrating with a standard solution of sodium hydroxide, using bromcresol-green as the indicator. Selenic acid should have but one pH break running from about 4 to 10 (Fig. 2). Knowing the normality of the selenious acid used and that of the selenic acid formed it was possible to calculate the per cent of selenious acid oxidized. By plotting the pH against the milliliters of base added a graph was obtained which showed that there was still some selenious acid present There were two pH breaks in the graph (Fig. 3). It is believed that


TITRATION OF SELENIC ACID
Figure II
12
10
8
6
4
2
0
40
80
120
160
MILLILITERS OF 0.1197 N. NaOH


TITRATION OF SELENIC ACID
AND SELENIOUS ACID MIXTURE
Figure III
pH
12
10
8
6
4
2
0
20
40
60
80
MILLILITERS OF 0.1197 N. NaOH

the first pH break was due to all the selenic acid and half the selenious acid that were present. More runs were made with increasing amounts of peroxide. It was shown that the same amount of peroxide was needed for this method of preparation as for the acid method of preparation. When the solution was allowed to stand for two hours before heating, the yield of selenic acid was a little better but still too low to be used. It was shown also that as the concentration of the base increased the oxidation of selenious acid increased, thus indicating that the hydroxide decomposed the hydrogen peroxide. Therefore, this method of preparation was also discarded as impracticable.

Determination of Cobalt

A standard solution of potassium selenocyanate was prepared by the method given in Inorganic Syntheses (4). After the potassium selenocyanate was crystallized, it was dissolved in acetone and stored in a glass stoppered flask. The solution was standardized by adding concentrated hydrochloric acid to a sample of the solution. This precipitated red selenium and gave off hydrogen cyanide vapors. The selenium was filtered, dried, and weighed. The concentration of the potassium selenocyanate could then be calculated.

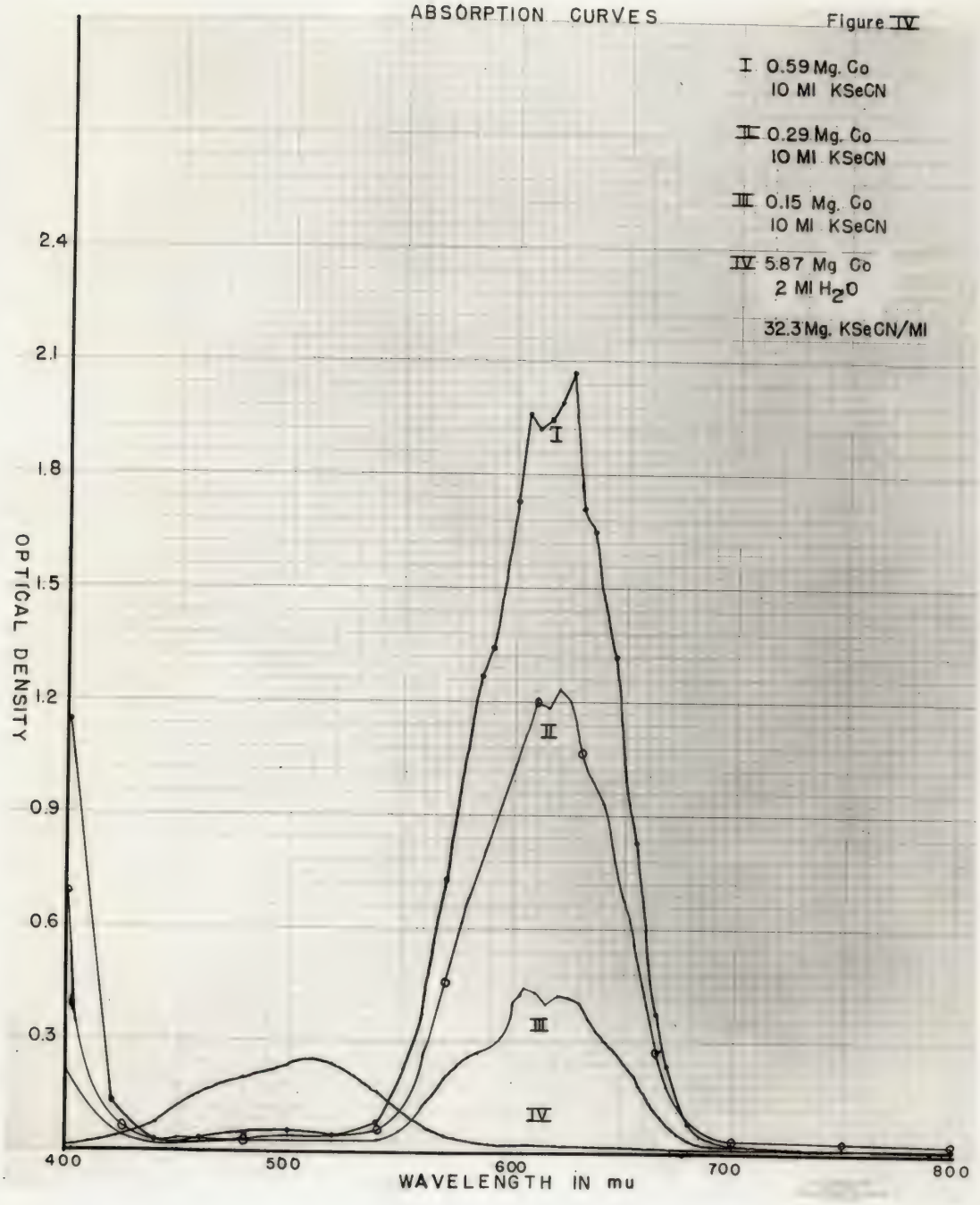
The solution of cobalt was made by weighing out an amount of cobalt sulfate and diluting to volume. The concentration of cobalt was checked by electrolytic deposition of cobalt on a platinum electrode.

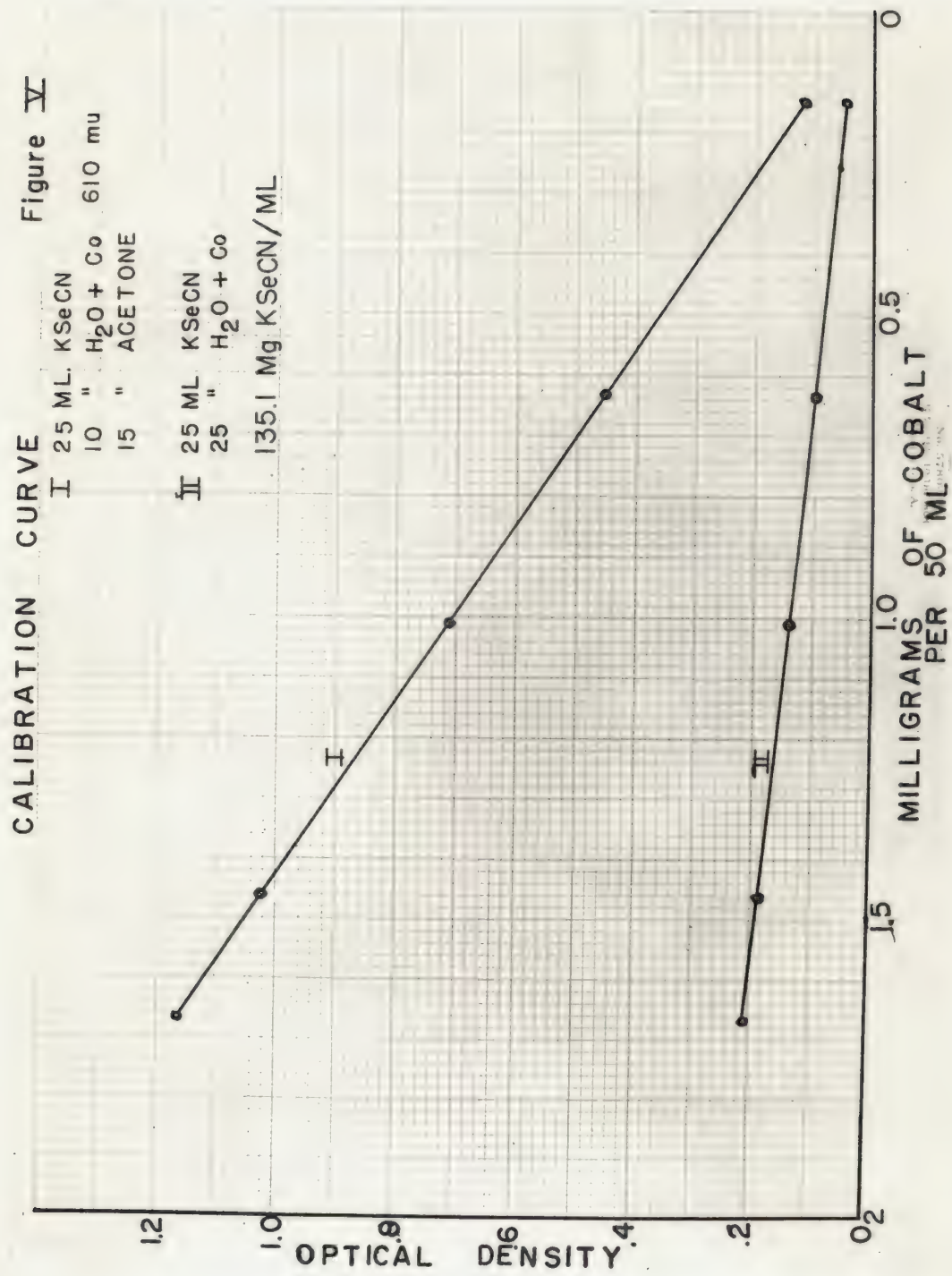
Complete absorption curves were obtained for varying concentrations of cobalt and the standard selenocyanate, cobalt and water,

and cobalt and potassium cyanide. The cobalt and selenocyanate, a blue solution, showed a peak at 610 mu (Fig. 4). The cobalt and water mixture showed a small absorption at 510 mu but not at 610 mu. The cobalt and potassium cyanide mixture showed no absorption at all. The spectrum was scanned from 400 to 800 mu. The cobalt and potassium selenocyanate showed another rise in absorption at 420 mu and was still rising at 400 mu. It may be that the mixture has another peak in the ultra-violet region of the spectrum or it may just rise to infinity.

The colored complex was investigated to see if it followed Beer's Law. Different amounts of cobalt were dissolved in 10 milliliters of water and added to 35 milliliters of the acetone solution of potassium selenocyanate. The mixture was then diluted to 50-milliliter volume with 15 milliliters of acetone. By plotting the optical density against the milligrams of cobalt per 50 milliliters of solution it was shown that a straight line resulted, proving that the complex followed Beer's Law (Fig. 5). The same series of cobalt concentrations were used to make up a similar solution except diluting with 15 milliliters of water instead of diluting with 15 milliliters of acetone. Although this resulted also in a straight line the values were considerably lower than those of the acetone solution. It is believed that these lower values were due to the greater dissociation of the complex in the water solution than in the acetone solution.

It was then necessary to study the effect of other ions on the complex. Copper, lead, magnesium, nickel, tin, ferrous and ferric, zinc and manganese were studied. Salts of these metals were weighed


ABSORPTION CURVES
Figure IV
I 0.59 Mg. Co
10 Ml KSeCN
II 0.29 Mg. Co
10 Ml KSeCN
III 0.15 Mg. Co
10 Ml KSeCN
IV 5.87 Mg Co
2 Ml H_2O
32.3 Mg. KSeCN/Ml
OPTICAL DENSITY
2.4
2.1
1.8
1.5
1.2
0.9
0.6
0.3
400
500
600
700
800
WAVELENGTH IN mu
I
II
III
IV


CALIBRATION CURVE
Figure V
I 25 ML. KSeCN
10 " H_2O + Co 610 mu
15 " ACETONE
II 25 ML KSeCN
25 " H_2O + Co
135.1 Mg KSeCN/ML
OPTICAL DENSITY
1.2
1.0
.8
.6
.4
.2
0
I
II
0
0.5
1.0
1.5
2
MILLIGRAMS OF COBALT PER 50 ML

and diluted to 100-milliliter volume. The blank remained the same as on previous runs -- 10 milliliters of potassium selenocyanate, 10 milliliters of water, and 10 milliliters of acetone for a total volume of 30 milliliters. A complete absorption scan was made of the solutions to see if they had a characteristic absorption peak. The cupric and ferric complexes showed some absorption at 610 mu but the other ions showed very little absorption there. The solutions are described in the tables below.

Table 1. The solutions of the interfering ions and potassium selenocyanate.

The complexes of	Solution	Precipitate
Lead salt	clear and faintly yellow	none
Cupric salt	red changing to colorless	red
Magnesium salt	colorless	white
Stannous salt	yellow	white, formed on standing
Ferric salt	colorless	red
Ferrous salt	colorless	red
Manganese salt	clear and colorless	none
Zinc salt	clear and faintly pink	none

Table 2. The solutions of the interfering ions and the cobalt-potassium selenocyanate complex.

Solution of	Solution color	Precipitate
Lead salt	remained blue	none
Cupric salt	remained blue	brown
Magnesium salt	remained blue	white
Stannous salt	greenish	white
Ferric salt	greenish	green
Ferrous salt	greenish	green
Manganese salt	remained blue	none
Zinc salt	remained blue	none

All the ions except zinc and manganese caused noticeable interference with the reading of the Beckman. On reducing the concentration of the ions it was found that lead caused relatively no interference when two milligrams or less was present. The remaining ions continue to show interference even in dilute solutions.

To check this method of determining cobalt 10 samples of a cobalt salt were weighed and dissolved in [illegible] milliliters of water. A potassium selenocyanate complex was then made with a 10-milliliter sample of this solution. A calibration curve was drawn and the amount of cobalt present in the 10 known samples was calculated in Table 3.

Table 3. The analysis of cobalt using potassium selenocyanate as complexing agent.

Sample	Weight of cobalt taken (mg)	Weight of cobalt found (mg)	Error (mg)
1	2.1	2.0	0.1
2	1.9	1.9	0.0
3	1.7	1.7	0.0
4	1.5	1.5	0.0
5	1.3	1.3	0.0
6	1.0	1.1	0.1
7	0.8	0.9	0.1
8	0.6	0.7	0.1
9	0.4	0.4	0.0
10	0.2	0.2	0.0

The effect of temperature on the complex was studied also. The optical density at 10° was 0.602, at 25° it was 0.585, and at 35° the optical density was 0.577. Therefore, it seems that strict control of temperature is not needed. However, there should be no large change in temperature.

The reproducibility of the method was checked by placing the same weight of cobalt salt in four solutions of the potassium selenocyanate and then taking the readings. Results are shown in Table 4. Although the first one is a little in error the other three samples are in very good agreement.

Table 4. The reproducibility of results.

Sample	Optical density	Weight of cobalt taken (mg)
1	0.745	1.1
2	0.740	1.1
3	0.740	1.1
4	0.739	1.1

DISCUSSION

The preparation of selenic acid proved to be impracticable, when potassium permanganate was used. The precipitate of manganic selenate was the determining factor when potassium permanganate was used. With different amounts of permanganate the amount of the precipitate remained fairly constant. However, with very large amounts of permanganate there seemed to be some manganese dioxide formed. It is believed that this was due to the decomposition of the potassium permanganate. The amount of manganic selenate formed remained the same.

The hydrogen peroxide method proved to be impractical because a large excess of 30 per cent hydrogen peroxide was needed to obtain complete oxidation of the selenious acid to selenic acid. Even with a 100 per cent excess of peroxide there was only about a 50 per cent oxidation. With larger excesses the amount of selenious acid oxidized increased to almost 100 per cent. The amount of ammonium hydroxide added also had an effect upon the amount of peroxide needed. The higher the pH the more peroxide was needed. This greater need for peroxide is due to decomposition of the hydrogen peroxide by the excess hydroxide. When the pH was kept below eight the percentage of selenious acid oxidized increased considerably.

The effect of the pH on the ion exchange resin is also worthy of note. When the selenic acid is first added to the resin the pH of the solution is high due to the ammonium ions present. As the acid passes down the resin column the ammonium ions are removed and the pH of the solution changes from seven to about one and a half

or two. As the pH of the solution decreases the capacity of the resin also decreases. The most effective pH range for this resin is 4 or above. Either another resin must be found that is effected less by pH change or a larger amount of Amberlite IR 120 must be used before one can be sure of removing all the ammonium ions from the solution.

The determination of cobalt using potassium selenocyanate seems to be valid. The method has its concentration limits but some adjustment can be made by changing the concentration of potassium selenocyanate. The increase in the concentration of selenocyanate raises the limit of cobalt concentration. The complex is definitely related to the relative concentration of the cobalt and selenocyanate. If the concentration of selenocyanate is too small the cobalt forms a compound that will precipitate from the solution. The concentration limit can be lowered by adding a known amount of cobalt.

Zinc and manganese cause no interference with the determination of cobalt. By keeping the concentration of lead small it will cause no interference. The other metals, copper, nickel, tin, magnesium and iron, must be removed. However, it would not be necessary to remove these metals quantitatively. If the concentration of the interfering ion is very low there will be little or no interference.

It is suggested that there might be a possible peak for cobalt, lead, iron, and copper in the ultra-violet region. All of these metals show an increase in absorption at 400 mu. However, it is possible that instead of a peak being formed they may go on to

infinity.

Indications are that this method is reproducible. The errors made in determining cobalt from the known solutions fall also within the experimental errors of weighing, dilution, graphing and the reading of the Beckman Spectrophotometer.

SUMMARY

1. Potassium permanganate was used to oxidize selenious acid to selenic acid but the yield was poor due to the precipitation of manganic selenate.

2. The hydrogen peroxide method cannot be used as a practical oxidizer of selenious acid because of the large excess of hydrogen peroxide needed to obtain a hundred per cent oxidation.

3. A method for determining cobalt using potassium seleno-cyanate as the complexing agent was established. The limits were found to be determined by the concentration of the potassium seleno-cyanate.

4. The interference of eight metals was studied and discussed.

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Appreciation is also expressed to all members of the Department of Chemistry who aided this work in any manner.

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Two methods of preparation for selenic acid were studied. The first using potassium permanganate as the oxidizing agent proved to be unsatisfactory due to the precipitate of manganic selenate. The potassium permanganate was added to a known amount of selenious acid, stirred for about three hours and then heated gently for a half an hour. The reddish-brown precipitate was allowed to settle before being filtered. The potassium and manganese ions were removed from the selenic acid solution by being passed through an ion exchange resin, Amberlite IR 100. A Bausch and Lomb large littrow spectrograph was used to show that the ion exchange resin removed the potassium and manganese ions.

The reddish-brown precipitate was checked for selenium, selenate and manganese content. Thirty per cent hydrogen peroxide was used as the solvent. Selenium was precipitated by making the solution acid with concentrated hydrochloric acid and adding solid sodium sulfite. Silver nitrate was added to precipitate the selenate as silver selenate. To precipitate the manganese the solution was made basic with ammonium hydroxide and the manganese was precipitated as a mixed oxide. The mole ratio of the selenium, selenate and manganese indicates that the precipitate was manganic selenate.

Hydrogen peroxide was used as the oxidizing agent in the second method of preparation. The solution was made slightly basic, pH 7-8.3, with concentrated ammonium hydroxide. A hundred per cent excess of three per cent hydrogen peroxide was slowly added with stirring. After a period of three hours the solution was heated to remove the excess ammonium hydroxide and hydrogen peroxide. The

ammonium ions were removed by passing the solution through another ion exchange resin, Amberlite IR 120. A modified Kjeldhal method was used to determine the effectiveness of the resin. This method of preparation was ineffective because of the excess of peroxide needed to obtain 100 per cent oxidation.

A colorimetric method of determining cobalt using potassium selenocyanate as the complexing agent was investigated. A complete scan of the absorption spectra showed that the complex of cobalt had a peak at 610 mu. A calibration curve plotting optical density versus the milligrams of cobalt proved that the complex obeys Beer's Law. It also showed that when water was used as the solvent instead of acetone there was less absorption. This was due to the greater dissociation of the complex in the water solution than in the acetone solution.

The interference of lead, copper, iron, tin, manganese, nickel, and magnesium were studied. Tin and manganese showed no interference with the complex. If the concentration of lead was kept below two milligrams it caused no interference. However, the other ions all showed interference with this method of determining cobalt. If the concentration of these ions are small enough it is believed that they will cause little or no interference.

While a change in temperature will cause some difference in the reading of the Beckman spectrophotometer no strict temperature control is needed. The reproducibility of results was very good. While the method has some concentration limits they can be extended by several devices. The concentration of the potassium selenocyanate

can be increased; a small portion of the unknown cobalt can be used or if the cobalt concentration is too small a known amount of cobalt can be added.